Semiempirical charge distribution of clusters in the ion sputtering of metal

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Abstract

We propose the generalization of a known established empirically (Wahl W. and Wucher A. Nucl. Instrum. Meth. **B 94**, 36(1994)) power law, describing relative mass-spectra of neutral sputtered clusters, on the cases of arbitrary cluster charges. The fluctuation mechanism of charge state formation of sputtering products in the form of large clusters with the number of atoms $N \geq 5$ is also proposed. The simple formula obtained by us has been shown a good agreement with the experimental data.

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Sputtering of solids under the ion bombardment is one of the main applied and fundamental problems which is importance in the many directions of contemporary science and technology. Considerable technological possibilities in the micro- and nanoelectronics, cosmic and thermonuclear technologies have stimulated increase of the number of works devoted to application and basic investigations of sputtering phenomenon (see, for example, recent reviews [1-3] and references therein). The theoretical description and estimations of sputtering processes are rather difficult due to the multiparticle character of problem both at the stage of ion penetration to solid and at the stage of formation sputtering products which consist of not only single target atoms but also polyiatomic particles, i.e., clusters. Presently, some perspectives on carrying out of "first principle" calculations are connected (see, also, estimates [4,5]) with computer simulation by molecular dynamics methods. However, such calculations are complicated in technical plan, especially in the case of increasing of the number of atoms in cluster and they are difficult for performing excluding the authors of these calculations.. The maximal using of possibilities of empirically established sputtering regularities is reasonable in this case. For cluster sputtering so-called power law for relative neutral cluster yield which was discovered experimentally (see for instance [6]) could be most important. According to this the norlmalized neutral cluster yield is described by the law N^{ξ}, where N is the number of atoms in the cluster and the parameter ξ depends on bombardment conditions and target type. One of most complex problems is also process of charge state formation of surface sputtering products. Considerable number of experimental and theoretical works are devoted (see, for example, review [7]) to the investigations of charge state formation of single atomic particles at the surface scattering or sputtering of metal surface. On other hand, the mechanism of charged structure formation

of polyatomic particles had been less investigated both theoretically and experimentally. In this paper the generalization of well known empirically established power law describing relative mass-spectra of neutral clusters for cluster emission of arbitrary charges is offered. The fluctuation mechanism of charge state formation of sputtering products in form of large clusters with the number of atoms $N \geq 5$ is also proposed. Derived simple formulas are in a good accordance with the experimental data. We use the old conception according to which large clusters are emitted as a whole agglomerate in the form of block of atoms (see also [8,9]) . We will consider the probability W_N of events corresponding to correlated movement of N -atomic block as given. Let us determine the charged state of the block of N-atoms. For this purpose we will follow the statistical deriving of Saha-Lengmuir's formula [10], and assume that with moving off of the cluster from the metal surface up to some distance (so-called critical distance) the exchange between the electrons of metal conduction zone and electrons of cluster atoms is possible. When cluster moves away from the metal surface to the distance exceeding critical one, the electron exchange stop unadiabatically. Further below saying about cluster electrons, we will mean valence electrons only and corresponding aggregate of states we will call the cluster conduction zone. We will also assume that namely between the zones of metal and cluster the exchange is possible. Then average number of electrons $\overline{n_\tau}$ on the energy electron level ε_τ of cluster, according to the Fermi distribution, is defined by $\overline{n_\tau} = \{\exp[(\varepsilon_\tau - \mu)/\Theta] + 1\}^{-1}$, where Θ is temperature, μ is the chemical potential. Let us denote via $\overline{\Delta n_\tau^2}$ the average of square deviation numbers of occupation n_τ from the equilibrium $\overline{n_\tau}$ - values. Then $\overline{\Delta n_\tau^2} = \overline{(n_\tau - \overline{n_\tau})^2} = \overline{n_\tau}(1 - \overline{n_\tau})$ [11]. Obviously, the average number of electrons is $\overline{N_e} = \sum_\tau \overline{n_\tau}$. Let the number of electron in cluster conduction zone is N_e. Then, according to definition, the average of square

deviation of number of electron in cluster conduction zone from average value is $\overline{\Delta N_e^2} = \overline{(N_e - \overline{N_e})^2} = \sum_\tau \overline{\Delta n_\tau^2}$. The cluster, having N_e electrons in conduction zone, will be electrically neutral, if $N_e = \overline{N_e}$, where $\overline{N_e}$ is the average number of electrons in the cluster conduction zone which is equal to the number of atoms in N -atomic cluster multiplied to valency γ (i.e., to the number of atomic electrons, yelding by neutral metal atom to the conduction zone). Thus, cluster charge is $Qe = (N_e - N\gamma)e$, where e is electron charge. Further calculations with these formulae require knowledge of the electronic structure of cluster and generally speaking cannot be performed in general form. However, if to consider cluster size is large enough and electronic states are quasi-continuous, one can exchange summing over the electronic states on integration over the zone [11]. Therefore, for the temperatures less than the degeneration temperature, i.e. for $\mu/\Theta \gg 1$, one has

$$\overline{\Delta N_e^2} \approx 2^{1/2} \frac{V m_e^{3/2}}{\pi^2 \hbar^3} \sqrt{\mu} \Theta \ ,$$

where m_e is electron mass in conduction zone, V is cluster volume and chemical potential of the degenerated Fermi gas with the number of particles $\overline{N_e}$ in the cluster volume V is [11]

$$\mu = (3\pi^2)^{\frac{2}{3}} \frac{\hbar^2}{2m_e} \left(\frac{\overline{N}_e}{V} \right)^{\frac{2}{3}} .$$

Thus, the average of square deviation of cluster charge from the equilibrium value of $\overline{Qe} = \overline{(N_e - N\gamma)e} = 0$, is [1]

$$\overline{(\Delta Q_N)^2} = e^2 \overline{\Delta N_e^2} = e^2 \frac{3^{\frac{1}{2}}}{\pi^{\frac{4}{3}}} \frac{m_e \Theta}{\hbar^2} \left(\frac{\overline{N}_e}{V} \right)^{\frac{1}{3}} V. \qquad (1)$$

[1] In principle, equality to zero of equilibrium cluster charge follows from the assumption that Fermi levels in cluster and metal coincide. If it is not executed, asymmetry between positive and negative charged clusters will be observed and corresponding changes in following formulas can be easy made.

Probabilities $P_N(Q)$ of values Q we will determine by making use of standard formula for probability of fluctuations, i.e.,

$$P_N(Q) = \frac{1}{D_N} exp\Big\{-\frac{1}{2}\frac{Q^2}{\overline{(\Delta Q_N)^2}}\Big\}, \tag{2}$$

where normalizing factor D_N is defined by summing (2) over all possible values (2) $Q = 0, \pm e, \pm 2e, ...$ Thus, to obtain probability W_N^Q of cluster emission with number of atoms N and charge Qe one should multiply the probability of occurrence of events W_N corresponding to correlated moving of N -atomic agglomerate, on $P_N(Q)$:

$$W_N^Q = W_N P_N(Q). \tag{3}$$

On other hand, according to experiment, neutral clusters are distributed by power law N^ξ, and so

$$W_N^{(Q=0)} = W_N P_N(Q=0) = N^\xi. \tag{4}$$

Thus W_N^Q can be written as follow

$$W_N^Q = \frac{1}{P_N(Q=0)} N^\xi P_N(Q). \tag{5}$$

As $P_N(Q=0) = 1/D_N$, then definitive expression for probability of N-atomic cluster emission and having charge Q will have a form

$$W_N^Q = N^\xi exp\Big\{-\frac{1}{2}\frac{Q^2}{\overline{(\Delta Q_N)^2}}\Big\}, \tag{6}$$

where, according to equation (1),

$$\overline{(\Delta Q_N)^2} = e^2 \frac{3^{\frac{1}{2}}}{\pi^{\frac{4}{3}}} \frac{m_e \Theta}{\hbar^2} \left(\frac{1}{d}\right)^{\frac{2}{3}} \gamma^{\frac{1}{3}} N \ , \tag{7}$$

where d is the number of atoms in the unit of cluster volume, i.e. concentration (which we have accepted equal to the atomic target concentration for numerical calculations).

Simplest characteristic of cluster charge distribution, consisting of given number of atoms N, is the ionization coefficient κ_N^Q which is equal to the ratio of number of clusters with charge $Q \neq 0$ and number of neutral clusters with the same number of atoms N. In our case ionization coefficient is

$$\kappa_N^Q = \frac{W_N^Q}{W_N^{Q=0}} = exp\Big\{-\frac{1}{2}\frac{Q^2}{\overline{(\Delta Q_N)^2}}\Big\}. \tag{8}$$

Obviously, our consideration is not applicable for the sputtering of single atoms or small clusters. From comparison with the experimental data one can made a conclusion (see also [8,9]) on applicability of the model beginning from the concrete number of cluster atoms ($N \geq 5$). In experiment one measures, usually, the relative probabilities of the cluster yield with different number of atoms. Therefore, to compare theoretical data with the experiment ones, one should at first divide the probability (6) to the probability of cluster emission with (6) $N = 5$ (more exactly, we can choose any value $N \geq 5$, but it is more conveniently for us, when $N = 5$) , i.e. $Y_N^Q = W_N^Q/W_5^Q$. The experimental data will be same normalized. Farther, if it is necessary, one can pass to arbitrary convenient system of units. The results of analysis of the general formulas and performed numerical calculations and experimental data which are given in Figs. 1-3 allow to come to the following conclusions: a) The charge state changes by the variation of target temperature, moreover the ionization coefficients increase by increasing of the temperature; b) relative mass-spectra of the neutral clusters do not depend on target temperature, while relative mass-spectra of charged clusters depend on it very strongly, but by increasing of temperature they approach to mass-spectra of neutral clusters; c) the more cluster charge, the more seldom they are found; for example, the number of clusters with charge 2, as a rule, less than the number of clusters with charge 1; d) large clusters are ionized in larger

degree; e) tendency to saturation of ionization coefficients with growth of cluster dimension is an important peculiarity, qualitatively the same behavior has been noted in experiments [12], that confirms the conclusions about coincidence of the relative mass-spectra of charged clusters with neutral ones, when values of N are large (i.e., when $N \gg 1$)). As it is well known, the experimental registration of the charged clusters is simpler technically than one of neutral clusters. Therefore the data of measurements of charged clusters allow restoring of neutral clusters distribution indirectly and experimental set up is simplified very much.

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Figure captions:

Fig.1. The dependence of coefficients of single and double ionization of clusters from 5 and 10 Ta-atoms on target temperature Θ.

Fig.2. The dependence of coefficients of single ionization on the number of atoms in cluster of Ag: dotted line - our calculations at target temperature $\Theta = 500^oK$, $\bullet$ - experimental data from [12].

Fig.3. Relative yield Y_N^1 of one charge cluster of Ta_N^{+1} in dependence on number N of atoms in cluster under one-charged ion of Au^{-1} (with the energy 6 keV) bombardment of tantalum at target and target temperature $\Theta = 2273^oK$: unbroken line - calculated values of Y_N^1, $\bullet$ - experiment [13].